

## Surface-Modified Polysulfone Hollow Fibers. II. Fibers Having $\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3^-$ Segments and Immersed in HCl Solution

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### Synopsis

Polysulfone ultrafiltration hollow fibers were chemically modified on the surfaces with propane sultone and  $\text{SnCl}_4$ , and immersed in HCl solution subsequently. The immersion of the fibers in HCl solution yielded lower molecular weight cutoff of the fibers than those without the immersion. The fiber, denoted as HP-SB-17H, rejected 5% of raffinose at feed concentration = 0.5 wt % and 14% of NaCl at the feed concentration = 0.0025 wt %. The rejection of NaCl for HP-SB-17H was found to increase with the decrease of the feed concentration, and showed the tendency of Donnan exclusion. The effective fixed charge density was estimated to be  $7.74 \times 10^{-4}$  eq/L for the fiber. Absorption of poly(ethylene glycol) and bovine serum albumin at pH 7.0 on nonmodified and modified fibers was estimated from the ratio of  $J\eta/J_0\eta_0$ , where  $J$  is flux,  $\eta$  is viscosity, and the suffix zero shows the values of pure water. The modified fibers with the propane sultone showed better results of antiabsorption than the nonmodified and conventionally sulfonated fibers in this study. This was attributed to the high flexibility of a sulfonated group originating from the existence of a joint segment of  $(-\text{CH}_2-)_3$  in the modified fibers.

### INTRODUCTION

Hydrophilic membranes such as cellulose acetate, poly(vinyl alcohol), and polyacrylonitrile membranes have superior characteristics of less absorption of solutes and lower molecular weight cutoff compared to hydrophobic membranes. The hydrophilic membranes, however, do not usually give thermal stability and have a susceptibility to chemical and bacteriological agents, whereas the hydrophobic membranes, i.e., polysulfone and polyimide, have the thermal stability and some chemical resistance.<sup>1,2</sup>

Surface modification of hydrophobic membranes<sup>1,3,4</sup> that introduce hydrophilic segments only on their surface may be a candidate idea to present both advantages of hydrophilic and hydrophobic membranes. The original characteristics of mechanical strength and thermal stability keep in the membranes,<sup>1,3</sup> since only the surface is modified. Transport characteristics are, on the contrary, governed by the hydrophilic skin layers in the membranes. In a previous study we introduced a new functional group,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3^-$ , on the surface of polysulfone hollow fibers from reaction among polysulfone, propane sultone, and Friedel-Crafts catalysts.<sup>3</sup> A hydrophilic sulfonate unit was located at the polymer chain having a joint segment of  $(-\text{CH}_2-)_3$  in this reaction and was regarded as a new modification of heparin active groups.

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In this paper we report that the modified fibers that were immersed in HCl solution result in lower molecular weight cutoff than originally surface-modified fibers. We compare and discuss absorption of poly(ethylene glycol) and bovine serum albumin on nonmodified polysulfone fibers, conventionally sulfonated polysulfone fibers, polysulfone fibers having  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3^-$  segments, and HCl-treated polysulfone fibers having  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3^-$  segments in this study.

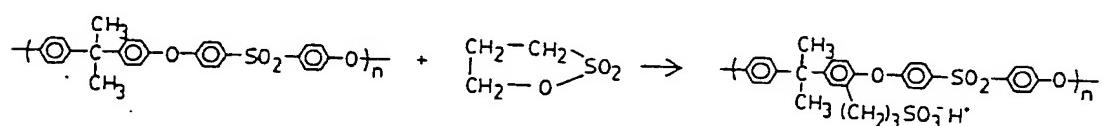
## EXPERIMENTAL

### Membranes

Membranes used for chemical modification were commercially available polysulfone hollow fibers (ultrafiltration membrane), SI-1 (Asahi Chemical Co., Ltd.), which is the same grade of fibers used in the previous study.<sup>3</sup> Water flux and rejection (*R*) of poly(ethylene glycol) 20000 for the fibers were observed to be  $14.5 \text{ m}^3/\text{m}^2 \text{ day}$  at  $3 \text{ kg}/\text{cm}^2$  and  $R = 0.126$  at concentration of feed solution = 0.5 wt % in this study.

### Chemical Modifications

The previous method of chemical modification of the fibers with propane sultone and  $\text{SnCl}_4$  catalyst was used to introduce  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3^-$  on the surface of the fibers:



Scheme 1

The reaction conditions are summarized in Table I. The surface-modified fibers were immersed in 0.5 N HCl solution for 1 min–50 h at 25°C, after the surface

TABLE I  
Surface Modified Conditions and Characteristics of Polysulfone Hollow Fibers\*

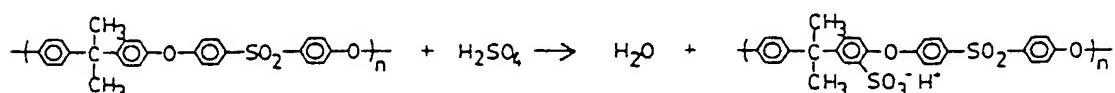
Membrane	Reaction temp. (°C)	Reaction time (min)	Modified side <sup>b</sup>	Mole ratio of PS to $\text{SnCl}_4$	HCl immersion time (min)	Rejection	Flux ( $\text{m}^3/\text{m}^2 \text{ day}$ )
HP-SI-4	50	15.0	I	0.37	No immersion	0.485	1.05
HP-SB-17H	50	10.0	B	0.50	2940	0.988	1.08
HP-SB-18H	50	5.0	B	0.37	3000	0.824	0.71
HP-SB-19H	50	10.0	B	0.22	3000	0.931	0.58
HP-SB-23H	50	30.0	B	0.22	2940	0.700	1.16
HP-SB-24H	50	10.0	B	0.37	10	0.314	0.39
HP-SB-25H	50	10.0	B	0.37	1	0.372	0.24

\* Catalyst =  $\text{SnCl}_4$ . PS stands for propane sultone. Ultrafiltration was performed on the conditions of feed solution = 0.5 wt % PEG 6000 at 20°C and  $\Delta p = 3 \text{ kg}/\text{cm}^2$ .

<sup>b</sup> I stands for the condition that the internal surface of the fibers is modified. B stands for the condition that the both surfaces of the fibers are modified.

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reaction was completed. Conventionally sulfonated polysulfone fiber (S-PSF-1) was obtained on the condition that the polysulfone fiber was immersed in 50 wt %  $H_2SO_4$  solution for 30 min at 25°C:



Scheme 2

## Transport Measurements

Ultrafiltration apparatus and procedures were described in the previous paper.<sup>3</sup> The trans pressure drop at the fiber,  $\Delta p$ , was fixed to be 3 kg/cm<sup>2</sup> throughout the experiments. Ultrapure water by Toraypure LV-10T system (Toray Co., Ltd.) was used throughout the experiments. The ultrafiltration measurements were performed at 20 ± 0.5°C. The standard deviations for flux and rejection measurements were found to be about 3 and 5%.<sup>3</sup>

## RESULTS AND DISCUSSION

## HCl-Immersed Fibers

Polysulfone hollow fibers were chemically modified on the surface according to the conditions shown in Table I. HP-SB-17 was immersed in 0.5 N HCl solution for 1 min–49 h. Dependence of rejection and flux on the immersion time of HCl at feed solution = 0.5 wt % of poly(ethylene glycol) 6000 (PEG 6000) is shown in Figures 1 and 2. It is found that the rejection curve in Figure 1 gives steep rise with increase of the immersion time until 60 min, and the fiber finally gives 98.8% of rejection after the immersion for 49 h (this fiber is

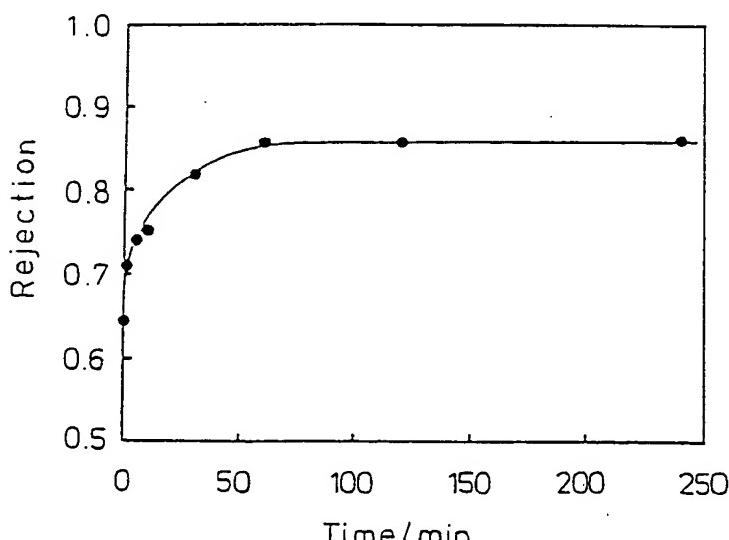


Fig. 1. Dependence of rejection on HCl immersion time for HP-SB-17 at  $\Delta p = 3$  kg/cm<sup>2</sup>. Feed solution is 0.5 wt % PEG 6000 aqueous solution at 20°C.

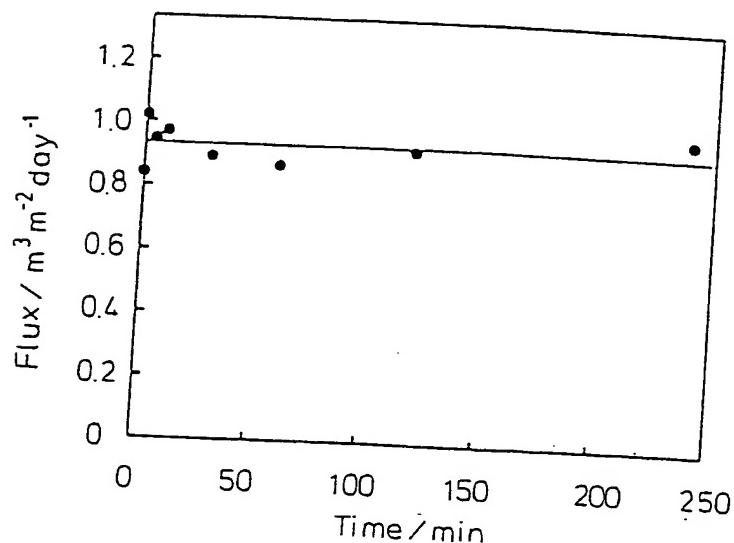


Fig. 2. Dependence of flux on HCl immersion time for HP-SB-17 at  $\Delta p = 3 \text{ kg/cm}^2$ . Feed solution is 0.5 wt % PEG 6000 aqueous solution at 20°C.

denoted as HP-SB-17H). The flux shows, on the contrary, no dependence on the immersion time within the experimental error and gives approximately 0.93  $m^3/m^2 \text{ day}$  for the fibers immersed in HCl solution until 250 min.

Figure 3 shows relationship between flux and rejection of PEG 6000 in chemically modified and nonmodified fibers at  $C_f = 0.5 \text{ wt \%}$ , where  $C_f$  is the con-

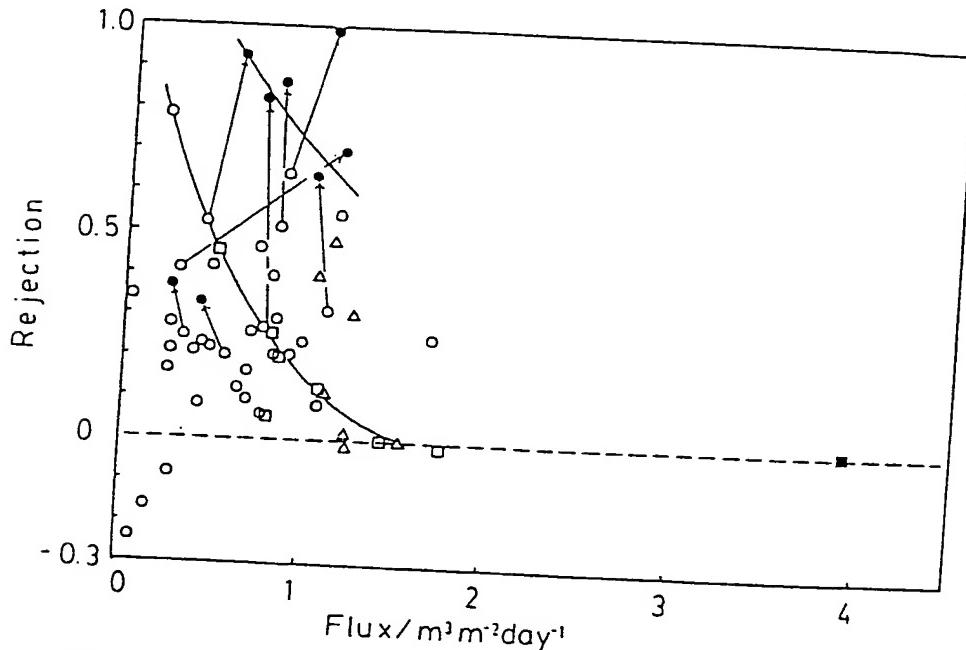


Fig. 3. Relationship between flux and rejection for chemically modified and nonmodified fibers at  $\Delta p = 3 \text{ kg/cm}^2$ . Feed solution is 0.5 wt % PEG 6000 aqueous solution at 20°C: (O) both surfaces modified with propane sultone and  $\text{SnCl}_4$ ; ( $\Delta$ ) internal surface modified with propane sultone and  $\text{SnCl}_4$ ; ( $\square$ ) external surface modified with propane sultone and  $\text{SnCl}_4$ ; (●) both surfaces modified with propane sultone and  $\text{SnCl}_4$ , and immersed in 0.5N HCl solution; (■) nonmodified fiber.

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centration of feed solution. Open symbols in the figure are the data for the fibers that are not immersed in HCl solution and include previously reported values.<sup>3</sup> Closed circles in the figure are data for the fiber after the immersion in the HCl solution. It is found that the fibers immersed in the HCl solution give higher rejection of PEG, and equal or higher flux than the originally modified fibers.

Rejections of several solutes in HP-SB-17H are summarized in Table II. HP-SB-17H was found to reject 5% of raffinose (MW = 504), which was not rejected by HP-SB-1 having lowest molecular weight cutoff in the previous study.<sup>3</sup> The molecular weight cutoff measured from 0.5 wt % of poly(ethylene glycol) solution is estimated to be 15000 for HP-SB-1 from previous study,<sup>3</sup> and 8800 for HP-SB-17H in this study.

Pore radius in the fiber can be estimated from the solute radius corresponding to its molecular weight cutoff. The solute radius  $r_s$  is estimated from the Stokes-Einstein relation<sup>5,6</sup>

$$r_s = kT/6\pi\eta D \quad (1)$$

where  $k$  is Boltzmann's constant,  $T$  is absolute temperature,  $\eta$  is the viscosity of water, and  $D$  is the diffusion coefficient.  $r_s$  for HP-SB-17H is calculated to be 20.8 Å for the solute of 8800 daltons of poly(ethylene glycol) having  $D = 10.3 \text{ cm}^2/\text{s}$ , which are taken from the literature.<sup>7</sup>

Rejection of NaCl for HP-SB-17H was measured as a function of  $C_f$ , and is shown in Figure 4. Rejection of NaCl is found to increase with the decrease of  $C_f$ , and shows tendency of Donnan exclusion of solutes in charged membranes.<sup>8-10</sup> The sulfonate group in the modified segments results in the generation of fixed charge in the skin layer of the fibers. Since NaCl (MW = 58.5) cannot be rejected from the pore size of HP-SB-17H, effective fixed charge density is estimated from eq. (2) with the assumption that NaCl is solely rejected by the Donnan exclusion in the skin layer. It is also assumed that NaCl permeate through the fiber only from mass flux and that the concentration of free ion in the skin layer is governed by coion concentration in the skin layer:

$$\begin{aligned} R &= 1 - C_- / C_f K \\ &= 1 - [V(C_x/2)^2 + (ZC_fK)^2 - C_x/2] / (ZC_fK) \end{aligned} \quad (2)$$

TABLE II  
Rejections of Some Solutes and Fluxes in HP-SB-17H at 20°C and  $\Delta p = 3 \text{ kg/cm}^2$

Solutes	MW/dalton	$C$ (wt %)	$J/m^2 \text{ m}^{-2} \text{ day}^{-1}$	$R$
PEG 6000	8400	0.5	1.08	0.988
Vitamin B <sub>12</sub>	1355	0.02	1.14	0.090
$\beta$ -Cyclodextrin	1135	0.50	1.11	0.202
PEG 600	600	0.50	1.24	0.138
Raffinose	504	0.50	1.22	0.046
NaCl	58.5	0.0025	1.29	0.140

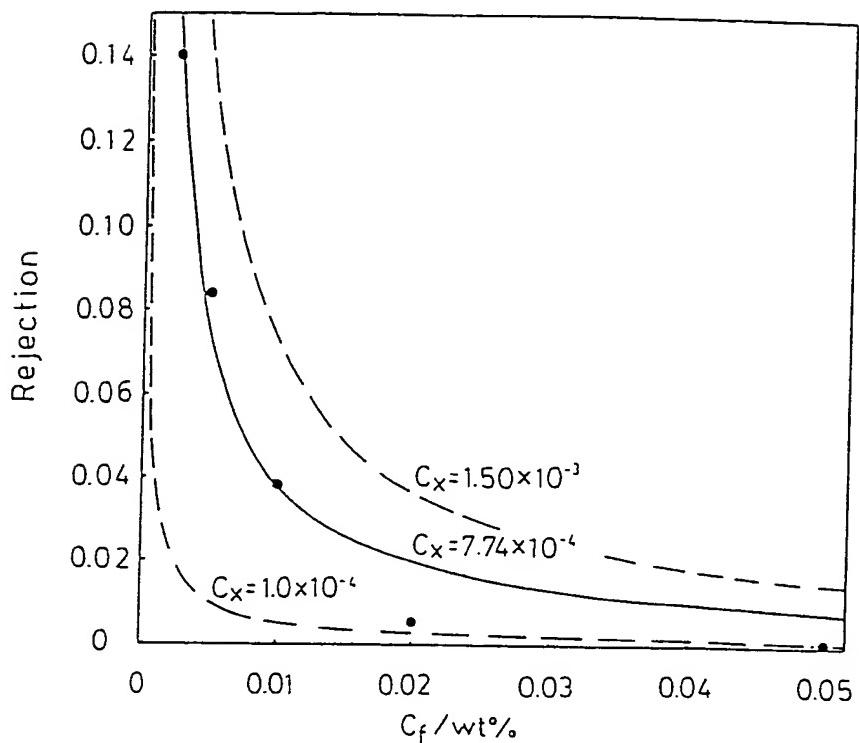


Fig. 4. Dependence of rejection of NaCl on feed concentration for HP-SB-17H at 20°C and  $\Delta p = 3 \text{ kg}/\text{cm}^2$ .

where  $C_-$  is anion concentration in the skin layer,  $K$  is the thermodynamic partition coefficient, and  $C_x$  is the effective fixed charge density.  $K$  is assumed to be unity in this case, since pore radius in the skin layer is approximately 20 Å and is large enough to think  $K = 1$ .  $C_x$  is obtained as  $7.74 \times 10^{-4} \text{ eq/L}$  from the best fitting of eq. (2) for  $R$  vs.  $C_f$  using the nonlinear least square method. The value of  $C_x$  for HP-SB-17H is observed to be considerably less than artificial membranes (i.e., 0.1 eq/L for Nafion membrane and 0.002 eq/L for carboxymethyl cellulose membrane<sup>11</sup>) and biological membrane (i.e., 0.12–0.17 eq/L for the capillary wall of the normal Munich–Wistar rat<sup>12</sup>). This is due to the fact that the pore radius is relatively large because of the ultrafiltration membranes, and the center of water in the capillary pores may permeate through skin layers without affecting the charge segments on the capillary surface.

#### Antiabsorption of Solutes

In a previous study we suggested  $J_\eta/J_0\eta_0$  gives a measure of the absorbed layer thickness of solutes on the pore wall, since  $J_\eta/J_0\eta_0$  is expressed as eq. (3) from Hagen–Poiseuille's law<sup>3</sup>:

$$J_\eta/J_0\eta_0 = r_s^4/r_0^4 \quad (3)$$

where  $r_0$  is the pore radius at no absorption of the solutes and  $r_s$  is the effective pore radius where the solutes are absorbed on the pore wall.

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Figure 5 shows dependence of  $J\eta/J_0\eta_0$  on feed concentration of PEG 6000 for nonmodified fiber (SI-1), conventionally sulfonated fiber (S-PSF-1), modified fiber (HP-SI-4), and modified and HCl immersed fiber (HP-SB-17H).  $J_0$  was reported to be  $8.05 \text{ m}^3/\text{m}^2 \text{ day}$  at  $3 \text{ kg/cm}^2$  using deionized water by Milli-Q system ( $15 \text{ M}\Omega \text{ cm}$ ) in the previous study,<sup>3</sup> whereas  $J_0$  is found to be  $14.5 \text{ m}^3/\text{m}^2 \text{ day}$  using ultrapure water by the Toraypure LV-10T system ( $18 \text{ M}\Omega \text{ cm}$ ) in this study.  $J\eta/J_0\eta_0$  for SI-1 is, consequently, calculated to be 0.260 at  $C_f = 0.5 \text{ wt \%}$  in this study, although  $J\eta/J_0\eta_0$  was reported to be 0.546 in the previous study.<sup>3</sup> It is found that  $J\eta/J_0\eta_0$  decreases with the increase of  $C_f$  for all four fibers until 2 wt % and gives approximately constant values at  $C_f > 2 \text{ wt \%}$ . Degree of absorption of the poly(ethylene glycol) is estimated to decrease in the following order, SI-1 > S-PSF-1 > HP-SI-4 > HP-SB-17H, from the figure without consideration of  $r_0$ . Present modified fibers by the propane sultone reaction are found to be excellent antiabsorption of poly(ethylene glycol) compared to not only the nonmodified fiber but the conventionally sulfonated fiber.

Figure 6 shows dependence of rejection on the feed concentration of PEG 6000 for the same fibers measured in Figure 5. The nonmodified fiber can reject 15% of PEG 6000 at  $C_f = 5 \text{ wt \%}$ , while the fiber rejects no PEG 6000 at  $C_f \leq 2500 \text{ ppm}$  within experimental error. The modified fibers show the similar tendency to the nonmodified fiber that the rejection increases with the increase of the feed concentration until a certain concentration. This effect can be explained by the coagulation of solutes in the dense solution and/or absorption of solutes on the pore wall. We believe that the latter effect is predominant in our study, and that the effect gives the smaller pore size than the original pore size. This effect is generally explained by gel layer model<sup>13-15</sup> or osmotic pressure model<sup>16,17</sup> due to cake formation<sup>18</sup> and concentration polarization.<sup>17</sup> The smaller pore size due to the absorption of solutes should be contributing to the decrease of flux with the increase of feed concentration as seen in Figure 5. It is found in Figure 6 that the rejection tends to gradual increase after a certain concen-

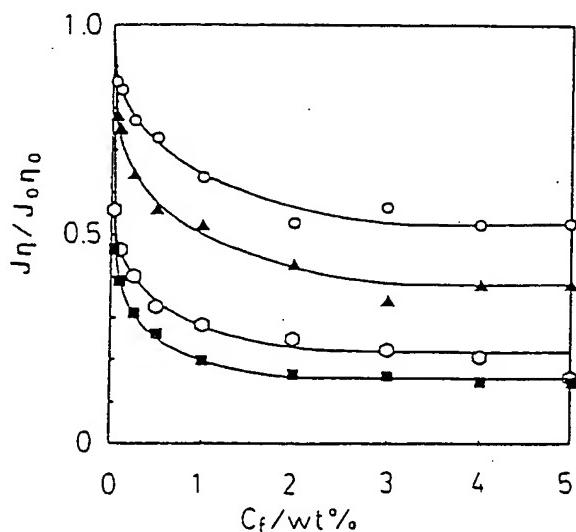


Fig. 5. Dependence of  $J\eta/J_0\eta_0$  on feed concentration of PEG 6000 for SI-1 (■), S-PSF-1 (○), HP-SI-4 (▲), and HP-SB-17H (○) at  $20^\circ\text{C}$  and  $\Delta p = 3 \text{ kg/cm}^2$ .

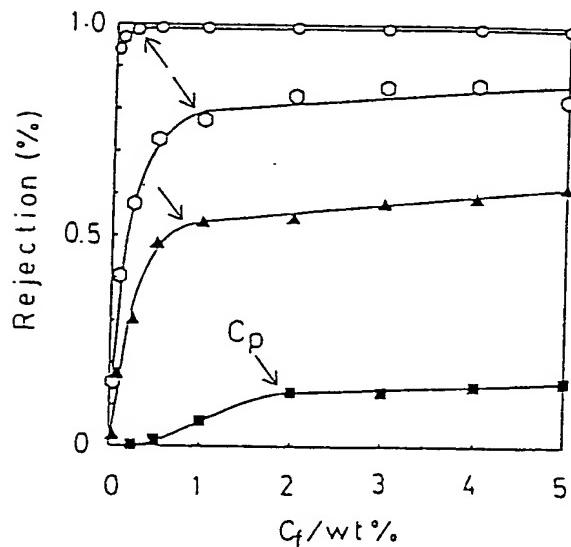


Fig. 6. Dependence of rejection of PEG 6000 on feed concentration for SI-1 (■), S-PSF-1 (○), HP-SI-4 (▲), and HP-SB-17H (○) at 20°C and  $\Delta p = 3 \text{ kg/cm}^2$ .

tration, i.e., 2 wt % for SI-1, 1 wt % for S-PSF-1, 0.8 wt % for HP-SI-4, and 0.25 wt % for HP-SB-17H. These points of concentration (denoted as  $C_p$ ) are shown as arrows in Figure 6. The  $C_p$  gives the same order (HP-SB-17H < HP-SI-4 < S-PSF-1 < SI-1) to that of the antiabsorption of PEG 6000 estimated in  $J\eta/J_0\eta_0$ . This is due to the fact that the fibers having the tendency of more absorption of solutes continue to absorb the solutes on the pore wall until the denser feed solution.

Rejection of solutes for S-PSF-1 is found between HP-SB-17H and HP-SI-4 in Figure 6. The original pore size of S-PSF-1 can be regarded as the intermediate size between HP-SB-17H and HP-SI-4. It is concluded that the modified fibers with propane sultone and  $\text{SnCl}_4$  absorb less solutes than the conventionally sulfonated fiber with no relation of the pore sizes in the fibers.

Absorption of bovine serum albumin (BSA) on the fibers is also tested in this study. Figure 7 shows dependence of  $J\eta/J_0\eta_0$  on time at  $C_f = 0.5 \text{ wt } \%$  of BSA in phosphate buffer solution at pH 7.0. The figure suggests that the modified fibers with propane sultone and  $\text{SnCl}_4$  give less absorption of BSA than the nonmodified and conventionally sulfonated fibers.

It is found that the fibers with propane sultone and  $\text{SnCl}_4$  have characteristics of antiabsorption of PEG and BSA compared to the nonmodified and conventionally sulfonated fibers. This effect can be attributed to the high flexibility of a sulfonated group originating from the existence of a joint segment of  $(-\text{CH}_2-)_3$  in the modified fibers.<sup>3</sup> The modified and HCl-treated fiber (HP-SB-17H) shows better results of the antiabsorption than the modified fiber without HCl immersion (HP-SI-4). The previous study shows the existence of residual catalysts in the modified fibers without HCl immersion from EPMA measurements.<sup>3</sup> The counterion of the modified fibers without HCl immersion should be mostly  $\text{Sn}^{4+}$ , and  $\text{Sn}^{4+}$  might contribute to the ionic crosslinking such as



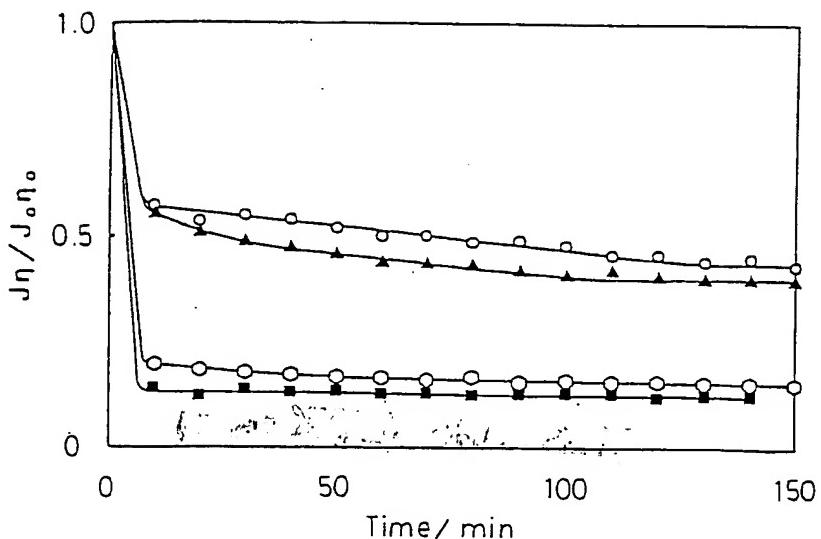


Fig. 7. Dependence of  $J\eta/J_0\eta_0$  on time for SI-1 ( $\blacksquare$ ), S-PSF-1 ( $\circ$ ), HP-SI-4 ( $\blacktriangle$ ), and HP-SB-17H ( $\circ$ ) at 20°C and  $\Delta p = 3 \text{ kg/cm}^2$ . Feed solution is 0.5 wt % BSA solution at pH 7.0.

The ionic crosslinking could be contributing to lose the flexibility of the sulfonated group to some extent. The residual catalysts should be rinsed out by HCl immersion of the modified fibers, and the removal of  $\text{SnCl}_4$  combined to the sulfonate group may result in much enhancement of mobility of the sulfonate group due to the removal of the ionic crosslinking. This would be the reason HP-SB-17H shows the highest antiabsorption behavior in this study.

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